Advances on Transition Metal Oxides Catalysts for Formaldehyde Oxidation: A Review

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Abstract

This review highlights recent advances in the development of transition metal based catalysts for formaldehyde oxidation, particularly the enhancement of their catalytic activity for low temperature oxidation. Various factors that enhance low temperature activity are reviewed, such as morphology and tunnel structures, synthesis methods, specific surface area, amount and type of active surface oxygen species, oxidation state and density of active sites are discussed. In addition, catalyst immobilization for practical air purification, reaction mechanism of formaldehyde oxidation and the reaction parameters affecting the overall efficiency of the reaction are also reviewed.

Keywords: formaldehyde, transition metal oxides, catalysts, oxidation

1. Introduction

Formaldehyde (HCHO) is one of the main sources of hazardous indoor air pollution. Furniture and building materials such as composite wood, particle board, vinyl coverings and adhesives are some of the major indoor sources of HCHO emissions (*1,2*). A comprehensive review of both the indoor and outdoor sources of HCHO and its concentrations in various indoor environments can be found in the work of Salthammer et al. (*3*). Exposure to HCHO may cause adverse health effects on humans such as irritation to eyes, nose and throat, headache, fatigue, edema, severe allergic reaction and dermatitis (*4,5*). In 2006, the International Agency for Research on Cancer (IARC) under the World Health Organization (WHO) classified HCHO as a carcinogen to humans. There are sufficient evidences to ascertain that it causes nasopharyngeal cancer and there are also strong indications that it may also cause sinonasal cancer and leukemia over long term exposure (*6*). As such there are various international guidelines and recommended thresholds for indoor air HCHO concentrations, a summary of which can be found in the review of Salthammer et al. (*3*). The WHO proposes a short term HCHO exposure limit (30 minutes) of 0.1 mg/m^3 for the avoidance of sensory irritation and a long term exposure limit of 0.2 mg/m^3 for protection against long term health effects (*7*). Thus, the effective removal of HCHO from indoor air is imperative to improving indoor air quality and safeguarding human health.

Various techniques for HCHO removal have been investigated and reported in the literature, including adsorption (*8-12*), photo-catalytic oxidation (*13-17*) and catalytic oxidation (thermal and non-thermal). The effectiveness of physical adsorption of HCHO on adsorbents such as activated carbon (AC) is constrained by the material's maximum adsorption capacity, relative humidity (RH) or moisture deactivation and also by the environmental risk when desorption occurs during regeneration (*18,19*). Photo-catalytic oxidation using ultraviolent light on the other hand may lead

to the generation of toxic by-products (*20*). Catalytic oxidation is able to achieve complete conversion of HCHO to H_2O and CO_2 without the formation of harmful by-products or secondary pollutants (*21*). This could even be achieved at room temperature especially with noble metal catalysts (*22-26*), thus making it the most promising HCHO removal technique (*18*).

Noble metal-based catalysts: Pt, Au, Pd, Rh, Ru and Ag supported on conventional materials such as TiO_2, SiO_2, Al_2O_3 and zeolites (*27-35*); single transition metals (*36-47*) and transition metal-based composites (*48-51*) exhibit excellent HCHO oxidation activities at temperatures lower than 100°C and even at room temperature. Comprehensive reviews on noble metal catalysts for HCHO oxidation have been conducted (*4, 25*), whilst here a summary of some of the noble metal catalysts and their reaction conditions are presented in Table 1. However, the industrial applications of noble metal catalysts are restricted by their high costs, limited resources and poor thermal stabilities (*53*). Hence recent research efforts have been focused on the development of relatively cheap materials for low temperature HCHO catalytic oxidation (*54-56*). More abundant and cost effective metal oxides especially those of the transition metals, including single transition metals and transition metal based composites are shown to be active for HCHO oxidation. However their relatively low activity compared to noble metals catalysts has motivated effort for further improvement. Therefore, the development of highly active and cost effective catalysts for HCHO oxidation is still a major challenge for practical application.

A number of review papers have been published on HCHO removal. Pei and Zhang (*52*) reviewed chemisorption method and catalytic oxidation of HCHO majorly on noble metal catalysts. The photo-catalytic oxidation of HCHO using TiO_2 as a photo-catalyst both in aqueous and gaseous mediums and the effects of different light sources and photoreactors have also been reviewed in a short article (*57*). More recently, Bai et al. (*4*) reviewed the catalysts for HCHO oxidation with a

major focus on the factors affecting the activity of noble metal catalysts. From the literature review, it can be seen that significant progress has been made on improving the activity of transition metal based catalysts and their immobilization for practical application since 2000. However, to the best of our knowledge, the development of transition metal based catalysts for HCHO degradation has not been reviewed in any detail so far. Therefore, we consider this review fills a key gap for this active area of heterogeneous catalysis.

This review focuses exclusively and extensively on recent developments over the past one and half decade towards enhancing the activity of transition metal catalysts for low temperature HCHO oxidation, considering their cost reduction potential, activity and stability. Various factors that enhance their catalytic activities are discussed, including preparation methods, morphology and structure, specific surface area, concentration of surface active oxygen species, oxygen mobility and metal active sites. The influence of reaction parameters such as relative humidity, HCHO concentration and space velocity are also reviewed. The reaction mechanisms of HCHO oxidation on transition metal oxides and their immobilization on suitable substrate materials for application in air purification are also elaborated and finally areas for further investigations to achieve higher activities at low temperatures are proposed.

2. Transition metal based catalysts and their performances

As mentioned earlier, recent research efforts have been focused on the utilization and efficiency improvement of transition metal based catalysts for low temperature oxidation of HCHO. Transition metal oxides are relatively cheap, abundant and have also been presented to be active for HCHO oxidation at low temperatures (*21*,*67*,*68*). Different terminologies such as HCHO removal, conversion, degradation and elimination are used in the literature to refer to the efficiency of HCHO oxidation. Hereinafter, efficiency of HCHO oxidation is referred to as conversion where

oxidation efficiency was reported as a function of CO_2 generation/concentration in the effluent stream and as removal where efficiency was reported based on residual HCHO concentration in the effluent gas stream (see footnotes of Table 1&2).

Some conventional transition metal-based catalysts have been reported to show good catalytic activities for HCHO oxidation. Sekine (*2*) first demonstrated the catalytic oxidation of HCHO over metal oxide catalysts. Of the investigated catalysts: CoO, MnO_2, TiO_2, CeO_2 and Mn_3O_4, MnO_2 was described to exhibit the highest catalytic activity. Metal oxides in the conventional bulk form possess low catalytic activity for HCHO oxidation owing to inferior surface properties (*69*). On the contrary, specially synthesized nanostructured transition metal catalysts of similar compositions to their bulk counterparts exhibit improved morphologies and surface properties and hence higher activities for HCHO oxidation (*21,70*). As such, current investigations on transition metal-based catalysts are focused on improving and developing materials with enhanced morphologies and structures. The structure of these catalysts and their morphologies improve their activity through the improvement of parameters (discussed in Section 4) such as specific surface area, high surface reducibility, porosity, active surface species, active lattice and surface adsorbed oxygen species and tunnel size and structure (*54,55*). Transition metal-based catalysts for HCHO oxidation found in the literature could basically be classified as single/mono-metal and composite metal oxides. A summary of both group of catalysts and their activities and conditions of reaction are respectively presented in Table 2 and 3.

2.1 Single transition metal based catalysts

2.1.1 Manganese oxide based catalysts

Manganese oxide is the most widely explored transition metal catalyst for HCHO oxidation owing to its high catalytic activity, thermal stability, existence in various crystal morphologies such as α-

, β-, γ- and δ-MnO_x (*71*) and several tunnel assemblies (1D tunnels, layered structures such as birnessite and buserite and 3D spinel tunnel structures) (*72*). Chen et al. (*55*) studied the influence of tunnel structures of various manganese oxide catalysts (pyrolusite, cryptomelane and todorokite) on HCHO oxidation. Cryptomelane displayed the highest activity with 100% HCHO conversion at 140°C, 400 ppm HCHO concentration, and a space velocity of 18,000 mL/g·h, while 20 and 40% conversions were attained by pyrolusite and todorokite, respectively, under similar reaction conditions. Tunnel size and structure were shown to be the determinant factors affecting activity other than factors such as specific surface area, degree of crystallinity, surface reducibility and average oxidation states of the catalysts. Similarly, Zhang et al. (*19*) attributed the high HCHO catalytic activity of δ-MnO_2 to its interlayer and tunnel structures which help in expediting adsorption and diffusion to and from the catalyst's active sites. These results indicate that activity is closely related to morphological and structural properties of the catalyst.

Tian et al. (*54*) investigated the impact of synthesis temperature on birnessite type manganese oxide catalysts. A general trend of catalytic activity rise was observed with increasing synthesis temperature from 80 to 120°C. The catalyst synthesized at 120°C exhibited the highest activity with a HCHO conversion of 100% at 100°C. This observed high activity was attributed to higher surface reducibility, specific surface area, crystallinity and porosity compared to other catalysts synthesized at different temperatures. Wang et al. (*73*) studied the effect of H_2O molecules on the activity of birnessite manganese for HCHO oxidation at room temperature and indicated that activity depends on the amount of both adsorbed H_2O molecules and interlayer hydroxyl and H_2O molecules present in the catalyst. Interestingly, as the drying temperature increases from 30 to 500°C, so does the specific surface area, but activity dramatically decrease as displayed in Figure 1(a) due to the reduction in water content. This result indicates that the activity of birnessite is

more a function of the interlayer H_2O molecule content than specific surface area. The presence of H_2O molecules enhances adsorption of HCHO molecules on the surface, conversion and desorption of intermediates from the catalyst's surface.

Furthermore, the effect of manganese vacancy (V_{Mn}) on the activity of birnessite-type MnO_2 was studied (*74*). Their results indicate that the presence of V_{Mn} improves the content of the surface adsorbed oxygen containing species facilitated by the presence of interlayer K^+, which helps in charge imbalance compensation caused by the created vacancy. The effect of surface pores created by the modification of birnessite-MnO_2 with nitric acid and tetra-ammonium hydroxide on HCHO oxidation was also investigated (*75*). The created defects as proposed by the authors served as sites for activation of molecular oxygen and H_2O, hence resulting in the increased density of active surface oxygen species and activity of the modified catalyst.

Tian et al. (*56*) also examined the effect of synthesis reaction temperature on the catalytic activities of various cryptomelane manganese octahedral molecular sieve K-OMS-2 catalysts. The K-OMS-2 nanoparticle catalyst prepared at room temperature exhibited a higher catalytic activity compared to K-OMS-2 nanorod structured catalyst prepared at 100°C. The former attained 64% HCHO conversion at the reaction temperature of 100^{o}C was due to the existence of a higher proportion of pore channels compared to the 10% accomplished by the latter under the same reaction conditions. Tian et al. (*36*) studied the relationship between textural properties and catalytic activity of the cryptomelane manganese oxide catalyst, and showed that a resultant increase in textural properties (specific surface area and pore volume) as a result of synthesis temperature increment from 15 to 70°C led to a dramatic improvement in catalytic activity.

147 Three dimensional mesoporous MnO_2 (3D MnO_2) catalysts prepared via nanocasting route using
148 KIT-6 hard template, which retain the mesoporous properties of the template were shown to be
149 promising for HCHO oxidation (*76*). The mesoporous structure, high specific surface area and
150 large number of surface active Mn^{4+} ions enhanced its high activity compared to the corresponding
151 α-MnO_2 and β-MnO_2 nanorod catalysts. Complete HCHO oxidation to H_2O and CO_2 was
152 accomplished at 130°C with 3D MnO_2 while same conversion was achieved at 140°C and 180°C
153 respectively with α-MnO_2 and β-MnO_2 under similar reaction conditions. This indicates that
154 activity is closely related to morphological structures of the catalyst. The catalytic activities of α,
155 β, γ and δ phase structures of MnO_2 were also investigated (*19*). The following order of activity
156 for complete HCHO oxidation was established: δ- > α- > γ- > β- MnO_2. Complete HCHO oxidation
157 was attained at 80°C on δ-MnO_2. Its high activity was suggested to be a function of its abundant
158 concentration of lattice oxygen species (see section 4.3 for further discussion on the roles active
159 surface oxygen species) and 2D layered structure, the latter of which enables easy adsorption and
160 diffusion of HCHO.

161 Chen et al. (*21*) prepared mesoporous hollow and honeycomb structured K_xMnO_2 nanospheres.
162 The former displayed higher activity of up to 100% HCHO removal at 80°C, while the latter
163 attained similar removal efficiency at 100°C under similar reaction conditions. Catalytic activity
164 of hollow structured K_xMnO_2 nanospheres was attributed to its porosity and the ability to retain
165 HCHO in its pores for a longer period compared to honeycomb structured catalyst. Zhou et al. (*77*)
166 examined the catalytic activity of various structures of Mn and the following order of decreasing
167 activity was established at reaction temperature below 120°C: cryptomelane Mn_2O > birnessite
168 Mn_2O > ramsdellite Mn_2O > monoclinic MnOOH. However, birnessite turns out to exhibit better
169 activity for complete HCHO oxidation at higher temperature, achieving 100% removal at 140°C

while cryptomelane at 160°C under similar conditions. This was possibly a result of weakened HCHO adsorption on cryptomelane at lower temperature as suggested by the authors.

2.1.2 Cobalt oxide based catalysts

Cobalt oxide is another important transition metal-based oxide that has recently been attracting attention for low temperature VOC catalytic applications. Similar to MnO_x, Co_3O_4 also exhibit various morphologies which include nano-fibers (*78*), nano-sheets, nano-cubes, nano-rods (*79*) and the morphologies influence its catalytic activity through the exposure of catalytically active surface sites (*70*). The activity of Nano-, 2D- and 3D-Co_3O_4 structures for complete HCHO oxidation was compared and the following order of reactivity was established: 3D-Co_3O_4 > 2D-Co_3O_4 > nano-Co_3O_4 (*70*). The superior activities of 3D and 2D-Co_3O_4 was ascribed to their mesoporous channel structure which enables easy diffusion of reactants to undergo reaction on the active surface compared to the non-porous nano-Co_3O_4; in addition, the best performance of 3D-Co_3O_4 was closely related to its abundant surface adsorbed oxygen species, large specific surface area and exposed active Co^{3+} species on the (2 2 0) crystal face. Similarly, Ma et al. (*51*) indicated that 2D-Co_3O_4 composed mainly of active Co^{3+} species on the (1 1 0) facet was able to achieve 20.3% HCHO oxidation at room temperature.

Fan et al. (*67*) investigated the effect of precipitants on the activity of Co_3O_4 catalysts. The catalysts synthesized using carbonates and bicarbonates displayed better textural properties and superior catalytic activities. The catalyst produced from $KHCO_3$ reached 100% HCHO conversion at 90°C, compared to 120°C and 130°C for those prepared from KOH and $NH_3 \cdot H_2O$, respectively. Recently, Wu et al. (*78*) described the utilization of porous Co_3O_4 nanofibers prepared by spiral electrospinning and controlled calcination (500°C) as highly active catalysts for HCHO oxidation. Complete oxidation was accomplished at 98°C under a space velocity of 30,000 mL/g·h and it was

shown to be highly stable for up to 160 hrs. Its activity was attributed to its high specific surface area and large pore volume which provided more active sites for the reaction.

Despite the reported influence of morphological structure on the activity of Co_3O_4 based catalysts, very few structures have been exploited for HCHO oxidation. There is therefore the need for further work to investigate other structures such as nano-sheets, nano-cubes, nano-rods and the extent to which they can influence other properties such as specific surface area, porosity and exposure of active metal sites and active oxygen species for improved low temperature HCHO oxidation.

2.1.3 Other metal oxides

Beside manganese and cobalt based catalysts, other metal oxides have been investigated in the literature. Xia et al. (*69*) synthesized 3D ordered rhombohedra Cr_2O_3 using assisted ultrasound nanocasting in the presence of 3D mesoporous silica (KIT-6) as template. The catalyst attained up to 90% HCHO conversion at 117°C. The ultrasound assisted synthesis played a major role in improving the characteristics and activity of the catalyst compared to similar catalysts synthesized in the absence of ultrasound. Huang et al. (*80*) first recounted the use of bifunctional Eu-doped CeO_2 with both thermal- and photo-catalytic oxidation capabilities for HCHO oxidation. Doping Eu onto CeO_2 dramatically enhanced its HCHO oxidation activity and complete oxidation temperature was reduced from 310°C on pure CeO_2 to 120°C on 4% Eu doped CeO_2. Catalytic activity was promoted through oxygen vacancy creation on the surface of CeO_2, greater redox ability, more abundant surface active Ce^{3+} and enhanced surface reaction. The created defects provide more sites for oxygen activation hence providing more active surface oxygen species for reaction. In addition, the catalysts exhibited an outstanding stability of up to 100 hrs on stream without any sign of deactivation. Similarly, Zeng et al. (*81*) demonstrated that hydrogenation

treatment of TiO_2 and C-TiO_2 improved their activity through the creation of more surface oxygen vacancy and surface hydroxyl groups. The untreated catalysts virtually displayed no activity for HCHO oxidation in a static chamber reaction after 4 hrs at room temperature in the absence of light illumination, while the treated catalysts including H-TiO_2 and H-C-TiO_2 were able to respectively attain 53% and 57% removal under similar reaction conditions.

In general, manganese and cobalt based catalysts were demonstrated to be active compared to other transition metals catalysts for HCHO oxidation. However, not much work has been done on other transition metals. In order to explore their full potentiality as viable catalysts, further work is needed to explore their utilization for low temperature HCHO oxidation. In addition, more work is required to explore surface oxygen vacancy or defects creation using various dopants to improve oxygen activation ability of metal oxide catalysts, to enrich active surface oxygen concentration for enhanced low temperature reaction.

2.2 Transition metal-based composites/mixed oxides

Transition metal-based composites have been widely applied in the control of pollutants such as CO (*83,84*) and ammonia (*85*). Composite catalysts for HCHO oxidation have also been investigated and reported in the literature. These catalysts are generated by co-synthesis of two transition metals oxides or the addition of other metal oxides either by co-precipitation (*48,86*) or by other synthesis methods such as nanocasting (*51*). Composite catalysts were shown to exhibit superior catalytic activities compared to the corresponding single materials synthesized using similar procedure. This is due to synergistic or promotional influence of improved oxidation capabilities either through higher surface oxygen mobility, creation of more oxygen vacancies (*48,86*) or enhancing charge transport during redox cycles (*87*). To improve oxygen vacancy formation in a composite catalysts and reduce the energy requirement for such, it was suggested

that the dopant should possess weaker M-O bonds; have larger radius and possess lower electronegativity (*88*). Various composites such as MnO_x-CeO_2 (*48,86*), Co_3O_4-CeO_2 (*51*), MnO_2-Fe_2O_3 (*89*), CuO-MnO_2 (*51,89*), MnO_x-SnO_2 (*90*), Co_3O_4-ZrO_2 (*91*) and Co-Mn oxide (*68*) have been studied for HCHO oxidation.

2.2.1 MnO_x-CeO_2 composites

The composites of Mn and Ce oxides were shown to be active for HCHO oxidation owing to the synergistic effect of Mn high activity and O_2 storage capacity of ceria. In addition, the composites aid in attaining higher oxidation states for Mn (*83,92*) which is vital for HCHO oxidation (*87*). Formation of solid solution between Mn and Ce is also critical to achieving synergistic influence through O_2 transfer mechanism (*48,86*). Solid solution was shown to be attained in the Mn-Ce molar ratio (Mn/(Mn + Ce)) range of 0.3 to 0.5, with 0.5 molar ratio being the optimum composition (*48,86,93*) and the solubility limit for the substitution of Ce ions by Mn ions in the composite (*53*).

Tang et al. (*86*) indicated that the manifestation of synergy in MnO_x-CeO_2 solid solution composite, which enables the composite to attain complete HCHO conversion at lower temperature (100°C) compared to pure MnO_x and CeO_2. The synergy was attained through a series of redox cycles (Mn^{4+}/Mn^{3+} and Ce^{4+}/Ce^{3+}) involving the activation of molecular oxygen by Ce and its transfer to Mn. The optimum calcination temperature for solid solution stability was shown to be 550°C, above which activity decreased owing to phase segregation. In another investigation, Tang et al. (*48*) further highlighted that above Mn-Ce molar ratio of 0.5, MnO_x crystallizes out of the solid solution, with a consequent drastic reduction in catalytic activity, which is in conformity with the findings of Li et al. (*93*). However, higher total decomposition temperature of 270°C was reported by Li et al. (*93*) for $Mn_{0.5}Ce_{0.5}O_2$. Nonetheless, the catalysts were able to totally oxidize

HCHO at room temperature in the presence of 506 ppm ozone (O_3) in the feed stream. The ozone molecules enhance the reaction by dissociating on the catalyst's surface and providing enough atomic oxygen species to drive the reaction (*93*).

Quiroz et al. (*53*) studied the impact of acid treatment over MnO_x-CeO_2 composite for HCHO oxidation. Their results indicated that the treatment had no pronounced effect on the textural and redox properties of the composites within the solubility limit of Mn (Mn molar ratio ≤ 0.5) in CeO_2. However, at higher Mn molar ratio (0.7 and 1) when MnO_2 began to crystallize out of the solid solution, significant improvement in catalytic activity was observed owing to the increased specific surface area and higher oxidation state of surface Mn. It is important to mention that while textural properties of the solid solution were not altered by the acid treatment, the oxygen transfer ability of CeO_2 was significantly hampered by the formation of $Ce(SO_4)_2$ resulting into a drastic reduction in activity. Therefore, acid treatment has positive effects on pure MnO_2 and an inhibitive effect on the synergy of the solid solution composites. The modification of birnessite-structured MnO_2 with ceria for HCHO oxidation was also reported in the literature (*94*). The incorporation of cerium ions inhibited the growth of MnO_2 crystals leading to particle size reduction and increase in specific surface area, as the amount of doped ceria increases. The doping led to the increase in the amount of oxygen vacancies and the rate of molecular oxygen activation into surface adsorbed oxygen species (O_2^-, O^- or terminal hydroxyl (OH) group (*74*)). The catalyst with the highest ratio of surface adsorbed oxygen to lattice oxygen exhibited the best catalytic performance. At higher ceria doping (Ce-MnO_2, molar ratio 5:10), the birnessite structure collapsed leading to decrease in catalytic activity.

Tang et al. (*48*) further demonstrated that impregnating Pt on MnO_x-CeO_2 composite significantly improved its activity by attaining 100% HCHO conversion at room temperature as shown in Table

1. It is noteworthy to mention that the formed composite (Pt/MnO_x-CeO_2) was prone to deactivation with increasing HCHO concentration. Its activity dropped from 100% conversion at 30 ppm to 54% in the presence of 580 ppm HCHO at room temperature as shown in Figure 2. Meanwhile the same authors (*86*) showed that MnO_x-CeO_2 composite was stable for complete HCHO oxidation over 48 hrs without any sign of deactivation at similar concentration (580 ppm). It should however be noted that the latter experiment was conducted at 100°C and the high temperature could aid the decomposition of intermediate species while the former was conducted at room temperature. This indicates that Pt might be prone to deactivation by HCHO at higher concentration, which needs to be investigated further.

2.2.2 Co_3O_4-CeO_2 composites

Ma et al. (*51*) investigated the oxidation of HCHO at room temperature on 2D-Co_3O_4-CeO_2 composites. They discovered that no synergy or activity improvement was realized by the formed 2D-Co_3O_4-CeO_2 composites and that 2D-Co_3O_4 was more active than the composites with respective HCHO conversions of 13.2% and 20.3% at room temperature. It should however be noted that no solid solution formation was observed in the 2D-Co_3O_4-CeO_2 composites, which is a phenomenon reportedly required for achieving synergy through ceria O_2 transfer mechanism (*48,86*). The incorporation of Au in the composite (2D-Au/Co_3O_4-CeO_2) improved the composite's activity to 50% conversion at room temperature (Table 1) by promoting desorption of surface active oxygen species (*51*). Liu et al. (*50*) presented the evidence of solid solution formation in 3D ordered macroporous (3DOM) CeO_2-Co_3O_4 catalysts with low loading of Co_3O_4. However, the 3D-CeO_2-Co_3O_4 catalysts with various Ce-Co molar ratios were shown to possess low catalytic activities. Loading Au particles (3 wt. %) on the composites distinctively improved their catalytic activities, and in fact all the Au supported composites were able to completely convert HCHO into

CO_2 and H_2O below 65°C. The composites (3D Au/CeO_2-Co_3O_4), with lower Co content in CeO_2-Co_3O_4 in the region solid solution, presented better activity in this study. When higher Co molar ratios was employed, segregation between CeO_2 and Co_3O_4 occurred, which led to weaker interaction and thus reduced the activity of the Au/CeO_2-Co_3O_4 catalysts.

2.2.3 Co-Mn oxides Composites

The composites of Co and Mn oxides were also studied and shown to be more active than the individual pure oxides for HCHO complete oxidation (*95*). Favorable synergy was obtained due to the abundant surface adsorbed oxygen species generated by the oxygen vacancies created in the Co-Mn oxides solid solution. Textural and redox properties were also shown to be affected by the synthesis method employed. Co-precipitation synthesis produced a more active catalyst with higher specific surface area, higher relative content of surface adsorbed oxygen species and surface active manganese (Mn^{4+}) that completely oxidized HCHO at 75°C compared to 100°C over that synthesized using sol-gel method.

Wang et al. (*68*) further studied the efficiency of the cycling "storage-oxidation" process for HCHO oxidation using 3D ordered mesoporous Co-Mn oxides composite (3D-Co-Mn) synthesized using KIT-6 template and that of Co-Mn oxides composite synthesized using co-precipitation. During the storage process, the catalysts were first exposed to a feed stream of O_2 and HCHO; subsequently, the stored HCHO was oxidized in a flow of O_2 at elevated temperature to evaluate its activity. The 3D-Co-Mn oxides composite was shown to have superior storage capacity of up to 0.8 mmol/g-catalyst and HCHO complete oxidation temperature of 70°C, compared to the storage capacity of 0.428 mmol/g-catalyst and HCHO complete oxidation temperature of 75°C respectively achieved by co-precipitated Co-Mn oxides composite. The

excellent activity of 3D-Co-Mn oxides composite was attributed to its larger specific surface area and ordered mesoporous structure. Lu et al. (*96*) studied HCHO oxidation over MnO_x-Co_3O_4-CeO_2 composites and found out that the incorporation of MnO_x into Co_3O_4-CeO_2 greatly improved its textural properties and the amount of available surface active oxygen species, resulting in an improvement in catalytic activity.

2.2.3 Other Composites

Other composites such as MnO_x-SnO_2 (*90*) and zirconia supported cobalt oxide catalysts (*91*) have been reported in the literature. Wen et al. (*90*) showed that the redox properties of MnO_x-SnO_2, which were in turn influenced by the preparation method, played a crucial role in determining its activity. Their experimental results highlighted that higher oxidation states of Mn were more active in HCHO oxidation. The dominant oxidation state of Mn in the composite synthesized using redox co-precipitation was Mn^{4+} while Mn^{3+} was the main state in the co-precipitated composite, which accounted for the difference in their activities as shown in Table 3. This is in agreement with other reported literatures for the active state of Mn for HCHO oxidation (*76,86*). Lu et al. (*87*) investigated the catalytic performance of graphene-MnO_2 (G-Mn) hybrid for complete oxidation of HCHO. The G-Mn hybrid catalyst achieved complete HCHO conversion at 65°C, compared to 140°C for pure MnO_2 and the completely inactive graphene (G) nanosheets. The hybrid system exposed more Mn^{4+} active sites, enhanced charge transport during Mn redox cycle and offered a larger amount of surface HYDROXYL species which eased HCHO oxidation and improved activity.

3. Catalyst immobilization on porous materials for practical HCHO oxidation

For practical applications, deployment of powdered form materials especially nanosized, gives rise to engineering challenges such as dust contamination and nanoparticle leaching in flue gas streams

(*82*). Therefore, catalysts immobilization on porous materials with low air pressure drop is considered viable for air purification processes. A variety of porous materials with low air resistance including polyethylene terephthalate (PET) (*18*), polyester particulate filter (*97*) and porous cellulose fiber (*82*) have been used as supporting materials for immobilizing nanoparticle catalysts for HCHO oxidation. A summary of the activity of these immobilized catalysts is presented in Table 4. Wang et al. (*18*) reported the in-situ coating of δ-MnOx nanosheet on the surface of PET first through surface reaction followed by in-situ deposition. The formed composite which is light with low air resistance and high specific surface area, proved highly active and stable for low concentration HCHO (0.6 mg/m^3) oxidation at room temperature for 10 hrs. Sidheswaran et al. (*97*) supported Mn based catalyst with 84% nsutite, 2% cryptomelane and 13% manjiroite composition on the surface of a thin polyester particulate filter for heating ventilation and air conditioning (HVAC) and evaluated its performance for HCHO oxidation. Experimental results indicated that stable single pass HCHO oxidation with over 80% removal efficiency at room temperature was achieved continuously for 35 days for both high and low face velocities close to typical building air ventilation systems.

Zhou et al. (*82*) likewise demonstrated an in situ deposition of MnO_2 nanosheets on cellulose fiber composite (8.86 wt.% MnO_2/cellulose fiber) and showed that even though birnessite powder is slightly more active than the composite (100% and 99.1% at 140°C, respectively), the composite is about 19 times more active in terms of HCHO removal per mg of MnO_2. However, the observed difference could supposedly be attributed to the removal/adsorption capacity of cellulose fiber and not necessarily HCHO conversion as CO_2 generation and catalytic activity of the cellulose fiber were not monitored in the experiment. Li et al. (*98*) and Dai et al. (*71*) respectively utilized AC for immobilizing birnessite-MnO_2. In both cases, HCHO was completely converted into CO_2 in a

static reaction chamber. However, the conversion patterns in the individual experiments were such that the concentration of HCHO sharply dropped in the first 60 mins with little corresponding CO_2 generation, possibly indicating that the molecules were actually adsorbed onto the surface of AC. The adsorbed molecules were consequently and slowly converted into CO_2 over 6 hrs (*98*) and 9 hrs on birnessite-MnO_2/AC (*71*) respectively as shown in Figure 3(a&b). Similar patterns were observed over unsupported birnessite as shown in Figure 1(b) (*73*). In contrast, simultaneous HCHO conversion and CO_2 generation were observed over modified birnessite with manganese vacancies and up to 81.7% conversion was attained in the first one hour of the static experiment (*74*). This indicates that the HCHO is instantaneously converted into CO_2, as opposed to the AC supported birnessite (*71,98*) in which the HCHO is adsorbed onto the AC and subsequently converted over time. Few immobilized transition metal-based catalysts for HCHO oxidation have been reported as presented in Table 4; therefore, further investigations are required to evaluate more effective substrate materials for immobilization and to understand their interactions with the catalysts and effectiveness for practical application in air purification process. In addition, these materials need to be tested under indoor conditions in air purifiers or HVAC systems and evaluate the effect of conditions such as particle leaching, dust contamination, relative humidity and temperature variation, on the effectiveness and stability of these materials.

4. Influence of catalyst based factors on HCHO oxidation efficiency

The effectiveness of HCHO oxidation process is majorly related to the activity/reactivity of the catalyst deployed and other reaction parameters such as temperature, concentration, space velocity, catalyst mass and relative humidity. Catalytic activity is in turn influenced by a number of physicochemical properties which include structure and morphology, preparation or synthesis method, degree of crystallinity, surface reducibility, specific surface area, amount of active oxygen

species and active metal sites (*54*). A combination of these properties is decisive for high catalytic activity and for an effective HCHO oxidation at low reaction temperature.

4.1 Influence of synthesis methods and conditions on textural properties, morphology and activity

Several conventional preparation methods can be used to synthesize catalysts for HCHO oxidation including sol-gel method (*56*), precipitation and co-precipitation (*86,97*). Recent researches have mainly focused on improving and modifying catalysts preparation methods to enhance their performance and catalytic activities through the utilization of synthesis techniques such as hydrothermal synthesis (*77*), electrospinning (*78*), electrodeposition (*80*) and hard template nanocasting (*70,76*). Synthesis methods and reaction conditions are able to tailor catalysts' textural and surface properties, structures and morphologies (as shown in Figure 4 (*77*)) and hence influence their catalytic activity (*36,54*) as shown in. For instance, the utilization of ultrasound assisted nanocasting of 3D-Cr_2O_3 using KIT-6 as template helps in enhancing the penetration of precursor materials into the mesoporous structure of KIT-6, which proved efficient in improving its specific surface area, pore volume and mesoporousity compared to 3D-Cr_2O_3 synthesized without the aid of ultrasound (*69*). Zhang et al. (*19*) highlighted that by varying reaction conditions in a hydrothermal synthesis, various crystal structures of MnO_2 including: α- and δ-MnO_2; β- and γ-MnO_2, with entirely different properties can respectively be produced from the same starting materials.

Reaction temperatures in hydrothermal synthesis have tremendous effects on morphology and structural evolution of structured manganese catalysts. Tian et al. (*54*) highlighted that the reaction temperature greatly affects the crystallinity, surface reducibility, specific surface area and activity of birnessite structured manganese oxide catalysts. At low synthesis temperature of 80°C, poorly

crystalline birnessites were produced, whilst the birnessites were transformed into well-crystalline structures when reaction temperature was increased to 100^{o}C, thereby increasing its activity. However, higher temperature (140°C) led to decomposition of the birnessite structure as a result of excessive reduction of Mn^{7+} by benzyl alcohol during the synthesis. Zhou et al. (*77*) also observed that birnessites structure obtained at 120°C synthesis temperature transformed into monoclinic MnOOH at 150°C and eventually collapsed into 1D MnOOH nanorods at 180°C as shown in Figure 4. Similarly, a correlation between synthesis temperature and catalyst's morphology for cryptomelane-type manganese octahedral molecular sieve (K-OMS-2) was reported by Tian et al. (*56*). The morphologies of the K-OMS-2 catalysts changed from nanoparticles at room temperature to nanorods at reaction temperatures of 80-100°C and to nanowires at 120°C.

Tian et al. (*36*) reported that essential properties of cyptomelane catalyst such as morphology, crystallinity, specific surface area and pore structure could be tailored by manipulating the hydrothermal synthesis temperature. Increasing synthesis temperature distinctively raised the crystallinity and textural properties of the catalyst. However, too high temperatures diminished crystallinity and this is in agreement with the findings of Tian et al. (*54*) for birnessite manganese catalysts. Textural properties such as specific surface area and pore volume were also shown to vary with the synthesis temperature. An increase in the synthesis temperature led to a dramatic improvement in textural properties: specific surface area and pore volume increased from 68 m^2/g and 0.2 cm^3/g at synthesis temperature of 15°C, to 206 m^2/g and 0.3 cm^3/g at 70°C, respectively. Such an improvement in textural properties in turn led to enhancement in catalytic activity.

Calcination temperature was also demonstrated to be very critical for catalysts structural stability and activity. Wang et al. (*73*) indicated that between 30 and 300°C only a little change was

observed in the sizes of birnessite nanospheres and that the structure was prevented from collapsing by interlayer K^+ and H_2O molecules present. However, when the calcination temperature reached up to 500°C, the layered structure of birnessite completely collapsed and transformed into cryptomelane with a 2 × 2 tunnel structure due to the loss of interlayer H_2O molecules. The calcination temperature of composite MnO_x-CeO_2 prepared using modified co-precipitation was shown to greatly influence its catalytic activity for HCHO oxidation (*86*). As the temperature rises from 300-500°C, the relative amount of surface active Mn^{4+} and lattice oxygen also rises, however at higher temperature (700°C) both the activity and the relative amount of lattice oxygen dramatically decreased due to phase segregation evident by the appearance of MnO_2 crystals in the otherwise solid solution composite. Likewise, Wu et al. (*78*) indicated that high calcination temperatures (600-800°C) led to the decrease in the activity of Co_3O_4 nanofibers as a result of aggregation growth and collapse of the catalyst's mesoporous structure.

The utilization of templates and surfactants in catalysts synthesis for HCHO oxidation is also attracting attention. When templates are deployed in catalyst preparation, the catalyst's structures and morphology could easily be manipulated to enhance their catalytic activities (*56,76*) and replicate the characteristics of the template materials used. While Shi et al. (*95*) demonstrated that Co-Mn oxides composites prepared using co-precipitation method were far more active than those prepared using sol-gel method, the same group (*68*) further disclosed that 3D mesoporous Co-Mn oxides synthesized using KIT-6 hard template possessed superior activity owing to their better textural properties. Similarly, the synthesis of 3D-Cr_2O_3 (*69*), 3D-Co_3O_4 (*70*) and 3D-MnO_2 (*76*) have been demonstrated using KIT-6 molecular sieve hard template for HCHO oxidation. The presence of the template improved the mesoporous structure and specific surface area and exposes more active sites thereby enhancing catalytic activity. Other mesoporous structures including 2D-

MnO_2 (*99*) and 2D-Co_3O_4 (*51,70*) have been prepared using SBA-15 hard templates, which turned out to be more active than the corresponding non-porous materials but less active than their 3D-counterparts. Furthermore, Tian et al. (*56*) highlighted that highly active nanoparticle cryptomelane (K-OMS-2) catalyst could be synthesized at room temperature with the aid of cetyltrimethylammonium bromide (CTAB) surfactants without necessarily the use of high reaction temperature as earlier reported (*36*).

Acidity of the reaction medium and the type of acid deployed in controlling the pH have significant effects on the morphology of manganese based catalysts. Chen et al. (*21*) showed that mesoporous hollow and honeycomb K_xMnO_2 nanospheres with varying properties and activities could be produced by varying the ratio of $KMnO_4$ and oleic acid during the synthesis process. Zhou et al. (*77*) revealed that introducing H_2SO_4 (decreasing the pH) into a reaction medium that would otherwise produce birnessite structured manganese led to the production of cryptomelane structured manganese. However, the type of anions present in the acid is also critical in determining the resultant morphology under similar conditions. While the addition of H_2SO_4 led to cryptomelane structure, addition of H_3PO_4 and HNO_3 produced birnessite and ramsdelite structured manganese, respectively as shown in Figure 4. This shows that different anions play dissimilar roles in channeling the mechanism of crystal formation towards a particular morphology.

4.2 Influence of catalyst's morphology on activity

Catalysts' morphology and structure play an important role in promoting catalytic activities. Control over the morphological structure of catalysts is able to influence other properties such as pore size, specific surface area and the exposure of available surface active sites. The activity of manganese oxide catalysts with square tunnel structures (pyrolusite, cryptomelane and todorokite)

491 is majorly affected by their tunnel sizes (*55*). Similarly the available surface active sites depend on
492 the nature of the catalysts. 3D- MnO_2 catalyst have more exposed Mn^{4+} on its crystal lattice plane
493 thereby improving its activity compared to the one-dimensional α-MnO_2 and β-MnO_2 nanorod
494 materials (*76*).

495 Chen et al. (*55*) investigated the effect of MnO_x tunnel structure on the active oxidation of HCHO
496 as shown in Figure 5. Three types of Mn tunnel structures were investigated including pyrolusite
497 with tunnel structure of ca. 0.23×0.23 nm^2, cryptomelane consisting of double edge sharing MnO_6
498 octahedral with tunnel diameter of ca. 0.46×0.46 nm^2 and todorokite composed of triple chains
499 edge-sharing MnO_6 with tunnel of ca. 0.69×0.69 nm^2. Experimental results indicated that
500 cryptomelane had the highest catalytic activity achieving 100% HCHO conversion at 140°C.
501 Cryptomelane possesses an effective tunnel diameter close to HCHO's dynamic diameter (0.234
502 nm) thereby allowing better adsorption and higher catalytic activity (*55*). Yu et al. (*41*) indicated
503 that the micropore channel structure of nest- and urchin-like MnO_2 improved their catalytic activity
504 by allowing better adsorption of HCHO compared to that of cocoon-like MnO_2 without mesopores
505 present despite having higher specific surface area.

506 Tian et al. (*54*) also highlighted that the presence of smaller catalytic pore sizes could extend the
507 residence of HCHO molecules in the catalyst's pores thereby improve its oxidation efficiency.
508 Correspondingly, the work of Tian et al. (*56*) underscored that the pore structures of nanoparticle
509 K-OMS-2 were readily accessible to HCHO molecules, enhancing higher adsorption and better
510 activity compared to K-OMS-2 nanorods with similar specific surface areas. Zhang et al. (*19*)
511 further highlighted that the 2D layered tunnel structure of δ-MnO_2 enhanced its activity through
512 facilitating the adsorption and desorption of HCHO to active sites compared to other structures (α-
513 , β- and γ- MnO_2). In another research, Chen et al. (*21*) stressed that catalyst's activity depends

514 more on its porosity and nanoplatelets crystal size than specific surface area. Mesoporous hollow
515 K_xMnO_2 nanospheres, which have smaller nanoplatelets size and specific surface area twice less
516 than those of its corresponding mesoporous honeycomb structure, achieved higher activity in
517 HCHO oxidation.

518 Wang et al. (*73*) showed that the structure of birnessite is such that it contains HYDROXYL groups
519 and H_2O molecules at the interlayer surface. The presence of these molecules greatly improved its
520 catalytic activity for HCHO removal even at room temperature. After the removal of both the
521 hydroxyl groups and H_2O molecules at high temperature, the birnessite structure collapsed and the
522 catalyst lost its high activity. Likewise, Sidheswaran et al. (*97*) indicated that the existence of H_2O
523 molecules in interstitial voids of MnO_2 based catalysts with varying composition of nsutite,
524 cryptomelane and pyrolusite contributed to its higher catalytic activity compared to 99% pyrolusite
525 catalyst which has smaller tunnel structure and lower H_2O molecules content in its interstitial
526 voids.

527 4.3 Roles of active surface oxygen in HCHO oxidation

528 It is reported in the literature that surface oxygen species either in the form of surface adsorbed
529 oxygen species (O_2^-, O^- or terminal hydroxyl (OH) group (*74*)) and lattice oxygen are critical to
530 the effectiveness of the catalytic oxidation of HCHO and other intermediates into CO_2 and H_2O
531 (*51,67,95*). However, there is a discrepancy regarding the respective roles of each type of oxygen
532 specie for HCHO oxidation over transition metal based catalysts. For example, Zhang et al. (*19*)
533 stipulated that since HCHO oxidation was shown to conform to Mars van Krevelen mechanism,
534 abundant lattice oxygen on the catalyst surface will lead to higher catalytic activity. They further
535 showed that the catalytic activities of four MnO_2 catalysts (α, β, γ and δ-MnO_2) are closely linked
536 to their respective amount of surface lattice oxygen (relative to surface adsorbed oxygen species)

and the following order of activity was established: δ- > α- > β- > γ- MnO_2. Similarly, Tang et al. (*86*) indicated that the catalytic activity trend of MnO_x-CeO_2 composite catalysts synthesized using various methods, followed the trend of their relative lattice oxygen content. Those richer in lattice oxygen relative to surface adsorbed oxygen presented better activity.

On the other hand, surface adsorbed oxygen species were shown to be directly involved in the activation of HCHO and its subsequent oxidation into CO_2 and H_2O (*74,75*). It was shown that the activity of layered birnesite-MnO_2 catalysts with surface pits corresponds to the relative amount of surface adsorbed oxygen species on the catalysts (*75*). The surface pits acts as vacancies for activation of molecular oxygen and or H_2O into surface adsorbed oxygen and the higher the relative amount of these species the better the catalytic activity. Wang et al. (*94*) contended that while surface adsorbed oxygen species participates in the oxidation reaction of HCHO, lattice oxygen species enhance their formation through its complex interaction with oxygen vacancy and molecular oxygen. Huang et al. (*80*) reported that the enhancement of the relative amount of surface adsorbed active oxygen species was achieved through the creation of surface defects by doping Eu on CeO_2. The created oxygen vacancies served as sites for oxygen activation into active superoxide (O^{2-}) species which could partake in surface reaction, hence enhancing the concentration of surface adsorbed oxygen and the catalyst's activity. Similarly, surface defects created on birnesite-MnO_2 catalysts served as pits for activation of molecular oxygen and H_2O into surface active oxygen species, hence increasing the surface density of these species leading to higher catalytic activity (*74,75*). Ma et al. (*51*) also underscored the role of surface adsorbed oxygen (O^{2-}, O^-) in HCHO oxidation over cobalt based catalysts. They showed that catalytic activity is closely associated to the ease with which active surface oxygen desorb from catalysts surface. They further demonstrated that catalytic activity can be improved by increasing the ease

560 with which surface active oxygen desorb from catalyst's surface through the incorporation of Au
561 nanoparticles into Co_3O_4-CeO_2 composite. Likewise, it was demonstrated that 3D-MnO_2 with
562 abundant concentration of surface adsorbed oxygen species which easily desorb from the catalyst
563 at lower temperature exhibited better catalytic activity compared to 2D- MnO_2 with lower surface
564 adsorbed oxygen species concentration and nano-Co_3O_4 with virtually no active oxygen species
565 (O^{2-}, O^-) present (*70*).

566 In addition, Lu et al. (*87*) indicated that surface adsorbed oxygen species (hydroxyl group) and not
567 lattice oxygen are responsible for the high activity of graphene-MnO_2 hybrid catalyst for HCHO
568 oxidation. They further pointed out that the abundant relative amount of surface adsorbed hydroxyl
569 group on the catalyst did not only improve its catalytic activity but also simplified HCHO
570 conversion pathway by direct hydroxyl ion oxidation of formate species to CO_2 without the
571 formation of CO intermediates. It was also shown that surface adsorbed hydroxyl groups were
572 directly involved in the room temperature oxidation of HCHO on the surface of birnessite, which
573 led to the formation of formates and carbonates (*73*). Similarly, Wang et al. (*18*) showed that the
574 high amount of surface adsorbed oxygen in the form of hydroxyl species were responsible for the
575 high HCHO oxidation activity of δ-MnO_2/PET at room temperature. Similarly, Fan et al. (*67*)
576 underscored that hydroxyl species on the surface of Co_3O_4 are the key active surface oxygen
577 required for the formation of dioxymethylene (DOM) species and their subsequent conversion to
578 formate species in HCHO oxidation process.

579 4.4 Influence of reducibility and active metal sites on catalysts surface

580 The surface reducibility of catalysts plays an important role in determining their catalytic activity.
581 It indicates the amount of reactive species on the catalyst's surface and their onset reaction
582 temperatures (*54*). It could also indicate catalyst's oxygen mobility, which might cause more

583 oxygen adsorption and further excitement to active oxygen species which participate in the
584 oxidation reaction (*19*). Tian et al. (*54*) indicated a correlation between reduction temperature and
585 catalytic activity for birnessite manganese based catalysts. The established trend disclosed that the
586 lower the catalyst's reduction temperature (higher surface reducibility), the higher its HCHO
587 oxidative activity and vice-versa. Tang et al. (*86*) presented that owing to solid solution formation,
588 MnO_x-CeO_2 catalysts possessed higher surface reducibility and better catalytic activity compared
589 to pure MnO_x and CeO_2. Furthermore, the catalysts' activity reduced as surface reducibility
590 decreased (high reduction temperature) with increasing calcination temperature because of phase
591 segregation. Xia et al. (*69*) also indicated that chromia catalysts with the highest reducibility
592 possessed the best HCHO catalytic activity. Similar trends was also reported for HCHO oxidation
593 over Co_3O_4 catalysts (*67*).

594 The active sites present on catalyst's surface are critical and key for determining activity. The
595 higher the concentration or availability of exposed active metal sites on catalyst's surface, the
596 better its HCHO oxidative activity. Bai et al. (*70*) presented that Co^{3+} ions are the surface active
597 state and sites of 3D-Co_3O_4 for HCHO oxidation. The (220) crystal plane of the catalyst is
598 majorly composed of Co^{3+} against the Co^{2+} present on the (111) crystal plane of nano-Co_3O_4,
599 thereby making it more active and achieving complete HCHO oxidation at lower temperature.
600 Similarly, Ma et al. (*51*) demonstrated that the (110) facet of 2D-Co_3O_4 which is mainly composed
601 of Co^{3+} is the key active facet for effective HCHO oxidation. High activity for HCHO oxidation
602 by 3D-MnO2 was attributed to the presence of high content of Mn^{4+} active sites on the exposed
603 (110) crystal plane surface (*76*). These exposed ions provided sufficient sites upon which the actual
604 oxidation reaction takes place, thereby improving its activity. It was also shown that Mn^{4+} is the
605 active state and site for HCHO oxidation for MnO_x-CeO_2 based composite and the catalyst with

606 the highest amount of Mn^{4+} possessed the best activity (*48,86,87*). Zhang et al. (*19*) also
607 highlighted that amongst their investigated catalysts (α, β, γ and δ-MnO_2), those with the highest
608 content of Mn^{4+} displayed the best HCHO catalytic activity. Improving the electrochemical
609 properties of catalysts was proven to enhance their catalytic activities. Lu et al. (*87*) established
610 that the charge transport ability and interfacial electron transfer of MnO_2 during Mn^{4+}/Mn^{3+} redox
611 cycle can be enhanced by incorporating graphene into MnO_2 (G-Mn hybrid), which was revealed
612 to improve the electrical conductivity of MnO_2 and decrease electron transfer resistance. In
613 addition, it offered high specific surface area and 2D plane structure for increased exposure of
614 metal surface active sites (*100*).

615 4.5 Influence of specific surface area on HCHO catalytic activity

616 Catalysts' specific surface area is an important parameter affecting HCHO catalytic oxidative.
617 High specific surface area could enhance adsorption of HCHO molecules onto the catalyst's
618 surface and help in exposing more surface active sites, improving surface lattice defect and oxygen
619 vacancy, thereby leading to abundant surface active oxygen species (*70,78*), which is a key
620 requirement for oxidation reactions. A correlation between catalyst's surface and activity was
621 established by Wu et al. (*78*) for Co_3O_4 nanofibers. Activity increase was observed with increasing
622 specific surface area and pore volume as the calcination temperature increased from room
623 temperature to 500°C, above which a decline in activity was observed due to the destruction of the
624 mesopores and the consequent decrease in specific surface area at higher temperatures. Tian et al.
625 (*36*) also demonstrated that higher specific surface area greatly enhanced catalytic activity for
626 HCHO oxidation. Nanoparticle cryptomelane catalyst, with specific surface area as high as 206
627 m^2/g and smaller uniform mesopores exhibited higher catalytic activity than the corresponding
628 nanorod cryptomelane catalyst with a specific surface area of 68 m^2/g. The high specific surface

area and small nanoparticle sizes improved cryptomelane activity by increasing the available surface active sites and more accessible pore channels for adsorption and desorption of HCHO molecules and reaction products respectively (*36*). Sekine (*2*) showed that fine MnO_2 catalysts with higher specific surface area (163 m^2/g) achieved higher HCHO oxidation compared to MnO_2 catalysts with a specific surface area of 61 m^2/g. Similarly, Tian et al. (54) also reported that birnessite structured manganese catalysts having higher specific surface area exhibited better catalytic activities compared to those with lower specific surface areas.

However, high specific surface area does not always translate into superior catalytic activities in HCHO oxidation reactions. The activity of birnessite-type MnO_2 was shown to be independent on the catalysts' specific surface area trend (*74*) but on the relative content of surface adsorbed oxygen species and the manganese oxidation state. The catalyst with the highest manganese vacancy had the lowest specific surface area but exhibited the best catalytic activity. Shi et al. (*95*) also demonstrated that the activity trend of Co-Mn oxides composite with varying Co/Mn molar ratios did not follow their specific surface area trend, and in fact the catalysts with the smallest specific surface area exhibited the best catalytic activity. Complete oxidation of HCHO was achieved at 75°C on Co-Mn oxides (molar ratio: 3/1) with specific surface area of 92 m^2/g while only 64% conversion was attained on Co-Mn oxides (molar ratio: 2/1) with specific surface area of 172 m^2/g at the same reaction temperature. The higher activity of Co-Mn (3/1) oxides was a result of increase in the relative amount of surface adsorbed oxygen species realized from the creation of solid solution by the incorporation of Mn into the lattice structure of Co_3O_4. Fan et al. (*67*) also showed that Co_3O_4 catalysts with high surface content of K^+, CO_3^{2-} and Co^{3+} exhibited better activity despite having relatively smaller specific surface area.

5. Effect of reaction conditions on HCHO oxidation efficiency

Reaction parameters for HCHO oxidation process such as temperature, relative humidity, reactants' space velocity and HCHO concentration play great roles in ensuring the overall effectiveness of the oxidation reaction. These parameters need to be optimized especially reaction temperature considering the potential application of the process (no harmful by-products generation), in order to realize practically effective HCHO oxidation.

5.1 Reaction temperature and time

Reaction temperature is critical in HCHO oxidation, and generally the efficiency of HCHO oxidation over catalyst improves with increasing temperature even though some highly active catalysts are able to achieve complete oxidation at room temperature. Most of the reported transition metal based catalysts attained complete HCHO oxidation at temperatures above 100°C (*21,36,55,67,73,82*) with very few below 100 °C (*19,21,73,87,95,98*). Figure 6 presents the conversion/removal efficiency of HCHO as a function of reaction temperatures over different catalysts. However, it does not provide a basis for comparison due to the differences in the initial HCHO concentration and feed flow rate employed in various experiments. This makes it difficult to evaluate the specific reaction rates (equation 1) (*74*) of variously reported catalysts for rational comparison. For static systems, experiments are normally conducted at room temperature; in which case HCHO oxidation becomes a function of time in addition to other factors catalyst based factors discussed earlier (section 4). Figure 7 presents HCHO removal efficiency over various catalysts as a function of reaction time. It can be seen in Figure 7 that long reaction time is required to achieve complete HCHO removal in static system. For proper comparison, other factors such as initial HCHO concentration and the mass of catalyst used should be taken into account.

In view of these, more investigations are required to improve the activity of transition metal based catalysts at low temperature in order to compete with noble metal based catalysts which could successfully oxidize HCHO even at room temperature (*48,101*).

$$specific\ reaction\ rates\ \left(\frac{\mu mol}{m^2.min}\right) = \frac{C_{HCHO} \div 22.4 \times F \times \eta}{S_{BET} \times m} \quad \text{..... (1)}$$

Where C_{HCHO} is the inlet HCHO concentration (ppm), F is the flow rate (ml/min), η is the percentage HCHO conversion (CO_2 generation), S_{BET} catalysts specific surface area and m is the catalyst mass.

5.2 Relative humidity

Relative humidity (RH) at moderate levels influences the efficiency of HCHO oxidation, however at higher RH competitive adsorption of H_2O molecules tend to block the catalyst's active surface hence impinging activity. RH also helps in replenishing the supply of surface active hydroxyl groups which are consumed during HCHO oxidation, via the reaction of H_2O vapor and surface active oxygen (O_2^-, O^-) (*73,102*). Wang et al. (*18*) noted that in the presence of 50% RH, H_2O vapor react with surface active oxygen to generate enough surface hydroxyl groups to sustain HCHO oxidation reaction at RT. H_2O vapor also helps in carbonates desorption from the catalyst's surface via competitive adsorption, thereby enabling recovery of catalytic activity (*73*). Wang et al. (*73*) indicated that RH in the range of 33% to 65% enhanced HCHO removal on birnessite structured manganese at room temperature. However at higher RH (92%), catalytic activity was impacted owing to competitive adsorption of H_2O molecules on the catalyst's surface. Similar effects were observed with MnO_2/PET (*18*): at 0% RH significant deactivation was observed due to the formation of formate species on the catalyst's surface; however at higher RH (50%), the catalyst remained active and stable while activity significantly dropped when the RH was further

raised to 80% due to competitive adsorption of H_2O molecules. This conforms to the findings of Sidheswaran et al. (*97*).

5.3 Feed flow rate and feed concentration

The significance of feed (reactants) flow rate in terms of gas hourly space velocity (GHSV) on catalytic oxidation of HCHO was also reported in the literature. GHSV can improve the efficiency of a fixed bed reaction system in two ways; at higher velocity, it will help to a certain extent in enhancing external mass transfer while at a lower velocity it increases the residence time of reactants in the reactor (*52*). It was however reported that the efficiency of HCHO oxidation reactions decreases with increasing space velocity (*39,69,70,101*) and vice-versa. In view of these, it could be insinuated that external mass transfer has little or no limitation on the efficiency of HCHO oxidation reaction, although an experimental evaluation on external mass transfer effect would be required.

In addition, HCHO feed concentration is another significant parameter for HCHO oxidation process. HCHO oxidation efficiency tends to decrease with an increase in the feed concentration. Chuang et al. (*28*) demonstrated that an increase in HCHO feed concentration led to a decrease in conversion at the same reaction temperature. Likewise, Tang et al. (*48*) reported that catalytic activity decreased with rise in HCHO feed concentration from 30 to 580 ppm and that the catalysts were more active and stable at lower concentration. Correspondingly, Li et al. (*98*) pointed out that MnO_2/AC completely lost its activity when exposed to 5 mg/m^3 HCHO feed concentration in 32 hrs, compared to its sustained HCHO oxidation efficiency of up to 70% for 80 hrs under a HCHO feed concentration of 0.5 mg/m^3.

6. Reaction mechanism of catalytic oxidation of HCHO

Understanding the reaction mechanism of HCHO oxidation over transition metal based catalysts is vital for the development of catalysts with high efficiency, low cost and good stability. Different catalysts for HCHO oxidation may exhibit varying reaction mechanisms because different intermediate species could be formed with various active oxygen species and surface active sites (*4*). Oxidation reaction of HCHO over some transition metals based catalysts were shown to conform to Mars-van Krevelen mechanism (*18,19,97*). In this mechanism, reaction proceeds via a two-stage redox reaction with an assumption of constant surface oxygen. The catalyst's surface is first oxidized by gas phase molecular oxygen to form surface adsorbed oxygen species which subsequently reduces the pollutant (*52*).

Sekine (*2*) proposed that HCHO oxidation on metal oxides catalysts proceeds first by adsorption on the catalyst's surface followed by decomposition through the formation of formate intermediates on the surface, then the intermediates are subsequently decomposed to H_2O and CO_2 as presented in equations (2-5) where g and a indicate gaseous phase and adsorbed species, respectively.

$$HCHO_{(g)} + O_{(a)} \rightarrow HCHOO_{(a)} \quad (2)$$

$$HCHOO_{(a)} \rightarrow HCOO_{(a)} + H_{(a)} \quad (3)$$

$$HCOO_{(a)} \rightarrow H_{(a)} + CO_{2(g)} \quad (4)$$

$$2H_{(a)} + O_{(a)} \rightarrow H_2O \quad (5)$$

Tang et al. (*86*) indicated the oxidation of HCHO over MnO_x-CeO_2 catalyst was attained through the effective transfer of oxygen species from CeO_2 oxygen reservoir to MnO_2 active state. This synergy is achieved through the effective activation of feed molecular oxygen and the transfer of

738 the activated oxygen to replace the released active oxygen species from MnO_2 which participated
739 in HCHO oxidation through a series of redox cycles involving Mn^{4+}/Mn^{3+} and Ce^{4+}/Ce^{3+} (*48,86*)
740 as shown in Figure 8.

741 Wang et al. (*73*) proposed three-step mechanism for HCHO oxidation on birnessite structured
742 manganese catalyst at room temperature as presented in Figure 9. The reaction first proceeds
743 through H-bond between HCHO molecules and birnessite bonded H_2O molecules. The adsorbed
744 molecules are then oxidized to formate and carbonates by structural hydroxyl species.
745 Subsequently, the consumed hydroxyl ions are replaced through the reaction between surface
746 active oxygen and H_2O molecules. An oxygen vacancy is then formed on the site of the consumed
747 surface active oxygen species, which further acts as a site for molecular oxygen activation to active
748 species for continuous reaction (*74*). Wang et al. (*68*) reported that only hydrocarbonate species
749 were observed on the surface of 3D-Co-Mn catalysts with no obvious formation of formate species,
750 probably due to the fast conversion rate of formate to hydrocarbonates on the catalyst's surface as
751 suggested by the authors. The hydrocarbonate species were totally decomposed at 70°C as reported
752 by Shi et al. (*95*) for Co-Mn.

753 Shi et al. (*95*) indicated that the mechanism of HCHO oxidation over Co-Mn oxides proceeds via
754 the formation of DOM and formate species as intermediates. During adsorption process, HCHO is
755 immediately converted to DOM as no HCHO molecules were observed on the catalyst surface at
756 room temperature. The active DOM species react with surface adsorbed oxygen species to form
757 formate species and part of them are further oxidized to hydrocarbonates. At higher temperature
758 (50°C), further oxidation of formate and degradation of hydrocarbonate species occur. At the
759 complete oxidation temperature of HCHO (75°C), only adsorbed H_2O molecules were observed,
760 indicating complete oxidation of all the intermediate species. Hence, formate oxidation and

761 hydrocarbonate decomposition are considered as the rate-limiting steps for HCHO oxidation over
762 Co-Mn oxides catalyst.
763 A reaction mechanism for 2D ordered mesoporous Co_3O_4, Au/Co_3O_4 and Au/Co_3O_4-CeO_2 at room
764 temperature had been proposed by Ma et al. (*51*) as depicted in Figure 10. In this mechanism,
765 formate species are first generated by the nucleophilic attack on the C-H in HCHO by surface
766 active oxygen on the (110) facet of Co_3O_4 (with Co^{3+} as the active state). The formate species are
767 further oxidized to bicarbonates by surface active oxygen species. Carbonic acid species are then
768 generated by the reaction of the bicarbonates and H^+, which are subsequently decomposed to CO_2.
769 In contrast, Fan et al. (*67*) indicated that hydroxyl groups were responsible for the immediate
770 oxidation of HCHO on the surface of Co_3O_4 and that DOM and formate species were observed as
771 the intermediates during the adsorption of HCHO on the catalyst's surface as previously reported
772 (*95*). However, the behavior of the catalysts at elevated temperature in the presence of O_2 was
773 influenced by the existence of K^+ ions on the catalyst's surface. In the presence of K^+ ions, DOM
774 species generated during the adsorption process are converted to formate species and formate
775 oxidation to bicarbonates becomes the key reaction step. It was proposed that hydroxyl groups
776 were generated from surface hydrolysis of K_2CO_3 and got consumed during the reaction. The
777 consumed hydroxyl groups were replenished by the H_2O molecules generated thus K_2CO_3 surface
778 hydrolysis was sustained and the reaction was accelerated. On the other hand, in the absence of
779 K_2CO_3 at elevated temperature (80°C) only few DOM species could be converted to formate
780 species due to the lack of hydroxyl groups on the surface of Co_3O_4, thus formate decomposition to
781 carbonates and bicarbonates became the key reaction step at ≥ 80°C. Here it could be observed
782 that the existence of K^+ on the surface of Co_3O_4 changed the reaction path from formate
783 decomposition to formate oxidation and continued supply of surface hydroxyl group necessary for

784 the oxidation reaction was sustained by K_2CO_3 surface hydrolysis thus promoting HCHO
785 oxidation. Similar promotion effects of K^+ was observed for Ag/Co_3O_4 (*46*), Na^+ for ceramic
786 honeycombs (*103*) and Na^+ for Pd/TiO_2 (*59*).

787 Lu et al. (*87*) proposed a reaction pathway for HCHO over graphene-MnO_2 hybrid catalysts. In
788 this mechanism, HCHO is first oxidized to form formate intermediates while molecular oxygen is
789 activated and transferred to active Mn sites through Mn^{4+}/Mn^{3+} redox cycle. Graphene being an
790 electrical conductor reduces electron transfer resistance and enhances the rate of charge transfer
791 between Mn^{4+} and Mn^{3+}, thereby improving the overall efficiency of the process. Thereafter, due
792 to the abundant amount of surface hydroxyl groups on the hybrid catalyst, formate species were
793 directly converted to CO_2 and H_2O, while the consumed hydroxyl ions were regenerated by the
794 produced H_2O molecules as reported by other authors (*67*).

795 The reaction mechanism of HCHO catalytic oxidation is intricate and varies with the type and
796 amount of surface active oxygen or hydroxyl species present. But generally, formate species are
797 key intermediates present on almost all transition metal based catalysts. Other species such as
798 DOM and hydrocarbonates are also reported as intermediates for HCHO oxidation. However, the
799 reported pathways for HCHO decomposition varied in the literature. In some mechanisms DOM
800 species are first generated followed by their conversion to formate intermediates, which are
801 subsequently oxidized to hydrocarbonates and finally CO_2 and H_2O molecules are generated by
802 hydrocarbonate decomposition. In other mechanisms, no DOM species are observed and formates
803 are directly oxidized to CO_2 and H_2O especially in the presence of high amount of surface hydroxyl
804 groups (*67*,*87*). The reaction mechanism of transition metal based catalysts for HCHO oxidation
805 is minimally reported in the literature. This prompts the need for further elaborate investigation
806 into the mechanism on various active transition metals especially as it relates to the surface

properties of these catalysts, and the specific role of hydroxyl and oxygen species and the promotional effects of alkali metals (Na^+, K^+) on the overall efficiency of the reaction. This will provide more information and offer the basis for the design of yet more active and cost-effective catalysts for practical application.

7. Conclusions and outlook

Formaldehyde is one of the most harmful indoor air pollutants as it has adverse effects on human health due to its toxicity and carcinogenicity. Techniques such as adsorption, photo-catalytic oxidation and catalytic oxidation have been used in HCHO removal. Adsorption removal is limited by the adsorption capacity of the adsorbents deployed and the hazard of HCHO desorption during regeneration while photo-catalytic oxidation produces hazardous by-products. Catalytic oxidation offsets these drawbacks and can achieve complete conversion of HCHO into CO_2 and H_2O molecules without the formation of hazardous by-products.

Noble metal based catalysts exhibit excellent low and even room temperature HCHO oxidation capabilities but their practical application is restricted by their cost and availability. Recent investigations focus on the use of relatively cheap and abundant transition metals oxides and improving their low temperature performance. More attention has mainly been focused on the improvement and exploitation of various structures and morphologies of manganese oxide catalysts due to its high activity yet with little attention on other transition metal catalysts. As such, more investigation needs to be done on the improvement of morphological structures, textural and redox properties of these materials.

For practical air purification application in air purifiers or building HVAC systems, substrate materials with low air resistance and pressure drop are required to immobilize catalysts to avoid

dust contamination and catalysts leaching into treated air stream. However, only a few substrate materials have been reported in the literature and hence the need for further evaluation of more materials to understand their interactions with the catalysts and effect on activity for pragmatic air purification process. In addition to the development of these materials, they need to be tested under real indoor environmental conditions in air purifiers to evaluate the effects of system conditions such as face velocity, dust particle contamination and particle leaching on the efficiency and stability of the catalysts.

No single property is decisive for catalytic performance of transition metal oxides for complete oxidation of HCHO but a combination of several factors which include specific surface area, metal oxidation state, adsorbed and surface oxygen species, structure and morphology of the catalyst. Improvement of the morphological structures of transition metal based catalysts relative to their conventional bulk counterparts enhances their catalytic activity through improvement of specific surface area, mesoporosity and exposure of surface active metals and oxygen species. The tunnel structure of catalysts enhances the rate of adsorption of HCHO onto the active sites for decomposition and the rate of product desorption from the sites to make them available for the next molecules. This is particularly promoted when the catalyst's effective diameter is close to the dynamic diameter of HCHO (*55*). Oxidation state of metals in the catalyst is also vital for determining activity and higher oxidation states seem to be more active; Mn^{4+} in the case of manganese and Co^{3+} in the case of cobalt were identified to be the most active states for HCHO activation. Several methods have been proposed for improving the oxidation sate of metal oxides which include modified synthesis, controlling calcination temperature and the relative molar ratio of component elements, to maintain solid solution stability in the case of composite catalysts (86).

851 The use of hard template materials has been proven effective in providing the plane structure for
852 improved exposure of more surface active sites and enhanced access to these sites.

853 Active surface oxygen and hydroxyl species directly participate in oxidizing HCHO molecules
854 and all other intermediate species into CO_2 and H_2O. The higher the concentration of these active
855 materials on the catalyst's surface the better its HCHO oxidative activity. The availability of
856 surface active oxygen species and the rate of molecular oxygen activation could be enhanced by
857 the formation of surface vacancy using dopants and formation of solid solution composites with
858 oxygen carrier materials. Recently reported works (*80,81*) indicated that creating oxygen surface
859 vacancy using dopants increases the activation rate of molecular oxygen to more active and
860 reactive oxygen species thereby providing more abundant oxygen species for HCHO oxidation.
861 However not much has been reported on surface vacancy creation and surface modification using
862 dopants on transition metal based catalyst for HCHO oxidation, thereby prompting the need for
863 further exploration. The use of oxygen carrier materials for composite formation on the other hand
864 improves the transfer rate of active oxygen from the rich oxygen sources of the carrier to the active
865 metal sites in a complete redox cycle. The formation of solid solution within the solubility limit of
866 the composite is critical to achieving synergistic effects either through oxygen transfer or oxygen
867 vacancy creation, above which phase segregation occurs and synergy is lost. Most of the reported
868 composites in the literature for HCHO oxidation focus on the use of CeO_2 as composite material
869 with little or no attention to other oxygen carriers.

870 Furthermore, enhancing the electrical conductivity of catalyst through the formation of hybrids or
871 composites with electrically conducting materials such as graphene (*87*) was shown to greatly
872 improve catalytic activity at low temperature. The hybrid system exposed more Mn^{4+} active sites,
873 enhanced charge transport during Mn redox cycle and offered higher content of surface hydroxyl

874 species, which eases HCHO oxidation and improves the catalyst's activity at low temperature.
875 However, very few studies have been reported for catalyst's electrical conductivity enhancement
876 using conductor materials for HCHO oxidation. Hence further investigation into the influence of
877 dopants and other conductor materials on the activity of transition metals based catalysts for
878 improved low temperature HCHO oxidation will be desirable. In addition to catalytic properties,
879 reaction parameters such as reaction temperature, relative humidity, space velocity and HCHO
880 feed concentration also affect the overall efficiency of HCHO oxidation. Relative humidity at
881 moderate levels helps in enhancing the availability of surface active hydroxyl groups via the
882 reaction of H_2O vapor and surface active oxygen but becomes detrimental at higher levels.

883 The reaction mechanism of HCHO is complex and depends on the type of catalysts, the oxidation
884 state and amount of active metals and the nature of surface active oxygen (adsorbed and or lattice)
885 present. Although further research is required to ascertain the respective role of each in HCHO
886 oxidation. Only a few mechanisms were reported for transition metal catalysts, as such further
887 investigation is required into the reaction mechanism especially as it relates to the catalyst's surface
888 properties and the role of surface active oxygen or hydroxyl species. But generally, formate
889 species, DOM and hydrocarbonates are the identified intermediates for HCHO oxidation on
890 transition metal based catalysts. However, the reported pathways for HCHO decomposition varied
891 in the literature. In some mechanisms DOM species are first generated followed by DOM
892 conversion to formate intermediates, which are subsequently oxidized to hydrocarbonates and
893 finally CO_2 and H_2O molecules are generated by hydrocarbonate decomposition. In other
894 mechanisms, no DOM species are observed and formates are directly oxidized to CO_2 and H_2O
895 molecules without the formation of hydrocarbonates especially in the presence of high amount of
896 surface hydroxyl groups.

Acronyms

1D	One Dimensional
2D	Two Dimensional
3D	Three Dimensional
3DOM	Three Dimensional Ordered Macroporous
AC	Activated Carbon
CTAB	Cetyltrimethylammonium Bromide
DOM	Dioxymethylene
GHSV	Gas Hourly Space Velocity
HCHO	Formaldehyde
HVAC	Heating Ventilation and Air Conditioning
IARC	International Agency for Research on Cancer
KIT-6	Korea Advanced Institute of Science and Technology-6
K-OMS-2	Potassium-Octahedral Molecular Seive-2
PET	Polyethylene Terephthalate
R	Specific Reaction Rate
Redox	Reduction-Oxidation
RH	Relative humidity
SBA-15	Santa Barbara Amorphous-15
TOF	Turnover Frequency
VOC	Volatile Organic Compounds
WHO	World Health Organization

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